density, and we should expect the diffusion effect to be pronounced. The electrode would get saturated with hydrogen and would offer a big back e.m.f.

Experiment shows that the initial drop is followed by a very sudden rise as the electrode dissolves.

Platinum-Black.—Owing to the prepared surface, the rate of recombination should be very great from the commencement. No gases, in fact, are evolved with alternating current.

Experiment shows that the electrode fall is more or less steady.

Summary.

The variation with time of the electrode potential drop of various metals has been examined both with direct and alternating current. An attempt has been made to interpret these variations as being due to oxidation and occlusion phenomena within the electrodes. The conclusions confirm the results of the previous investigation on the volume of gases evolved during alternating current electrolysis.

We desire to express our thanks to Dr. E. H. Griffiths, F.R.S., for his interest in the paper, and to Mr. W. H. Sewell for his assistance in taking the observations.

Variation of the Intensity of Reflected X-Radiation with the Temperature of the Crystal.

By Ivor Backhurst, B.Sc.

(Communicated by Sir William Bragg, K.B.E., F.R.S. Received August 29, 1922.)

On account of the increasing importance of the temperature factor in the theory of the analysis of crystal structure by means of X-ray reflection, and in view of the fact that no experimental work on the temperature effect has been published since the original preliminary investigation by Prof. W. H. Bragg[*] in 1914, it is hoped that the present account will be of interest, in which the work of Bragg is extended to a variety of crystals and continuous temperature curves have been obtained ranging up to 950° C.

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[*] See "X-Rays and Crystal Structure," by Sir William Bragg and W. L. Bragg, also 'Phil. Mag.,' May, 1914.

Theories of the effect of temperature on X-ray reflection have been given by C. G. Darwin* and P. Debye,† and these agree in that the intensity of reflection—

(1) Decreases as the temperature of the crystal increases;
(2) Decreases more rapidly as the angle of reflection increases.

These conclusions, which can be arrived at by general considerations if it is assumed that the diffracting centres are in motion due to heat, are supported by the experiments of Bragg, and also by those here described, in which, with the notable exception of the sapphire and ruby, the intensity of higher order spectra has been found to diminish more rapidly with rise of temperature than that of lower order.

The method of experiment adopted by Bragg was to place the crystal inside an electric heater, furnished with mica windows suitably placed to allow of the ingress and egress of the X-rays, and provided with a thermometer arranged so that its bulb was immediately above the crystal. Intensities of the several orders of the reflection from different planes of rock-salt and sylvine were compared at room temperature and at 370° C. and 311° C. respectively.

In the present research a similar method was employed, the electric heater used being constructed to admit of a higher temperature range and the introduction of a nitrogen atmosphere, while a thermocouple was used to indicate the temperature of the crystal. It was also found necessary to use a special type of mounting for the crystal, in order to prevent rapid loss of heat by conduction, and at the same time allow of freedom of adjustment. Experiments were made with a number of crystals, and among these, aluminium, carborundum, graphite, diamond, sapphire and ruby furnished definite results which, while of the same order as predicted by theory, do not show good numerical agreement with the latter. This general result is the same as that arrived at by Prof. W. H. Bragg.

Aluminium.—In figs. 1 and 2 are shown the curves obtained for aluminium using molybdenum K-radiation, the width of the bulb, crystal and ionisation chamber slits being in each case 2 mm. The crystal reflection was integrated at a uniform rate over the whole angular range for which reflection occurred, half a degree being found sufficient in each case. The leak shown represents the deflection obtained when the ionisation chamber was just out of alignment. A considerable number of crystals were tried, many being unsatisfactory, as they gave progressively smaller reflections on repeated heatings, indicating a breaking down of the one complete crystal into smaller ones differently oriented.

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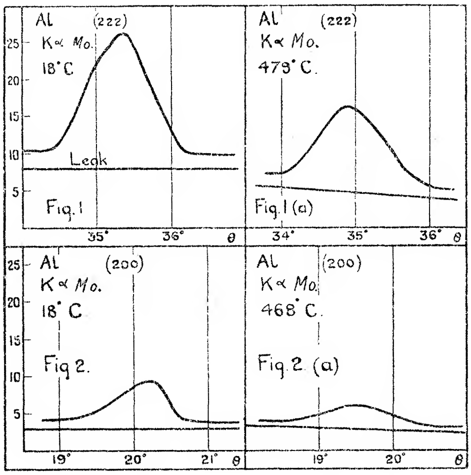
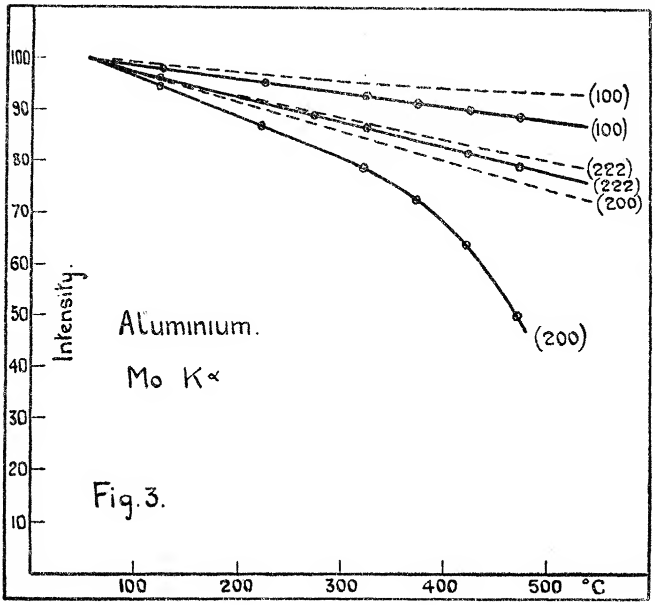
* 'Phil. Mag.,' February and April, 1914.
† 'Annalen der Phys.,' vol. 43, p. 87 (1914).



In fig. 3 the intensity for the reflection in question is taken as being 100 at 50° C., the ordinates to the continuous curves representing the corresponding intensities at higher temperatures. The points are each obtained by taking the mean of a series of observations, first for 50° C., then for the temperature indicated, then for 50° C., and so on; only the results for crystals giving consistent series of ratios being retained. The ionisation



chamber was set to take in the whole beam, and the reflection from the crystal integrated as in the original method. The deflection so obtained was taken to represent the combined intensity of the characteristic beam and the heterogeneous radiation. The intensity of the heterogeneous radiation was taken to be the same as that in an equal angular range just beyond the range of the characteristic radiation. To obtain this measure of the heterogeneous radiation, the crystal stage and ionisation chamber were moved to the proper positions and the reflection integrated as before, the difference between the two deflections being taken as proportional to the intensity of the characteristic radiation.

Owing to the expansion of the crystal, the position of the ionisation chamber had to be varied with the temperature.

Values obtained are given below :—

Temperature (t° C.).	Intensity (I).	Alteration of glancing angle $\theta/2$.
	(100) plane $\theta/2 = 10^\circ\ 4'$.	
50	100·0	0′
118	98·1	1′
218	96·0	3′
318	92·8	4′
368	91·0	5′
418	90·5	5′
468	88·9	6′
	(222) plane $\theta/2 = 17^\circ\ 40'$.	
118	96·6	3′
268	88·8	7′
318	96·7	8′
418	82·6	11′
468	79·9	13′
	(200) plane $\theta/2 = 20^\circ\ 28'$.	
118	95·3	3′
218	87·4	7′
318	80·1	10′
368	73·8	11
418	64·0	13′
468	50·8	15′

The expression obtained by P. Debye* for the temperature variation of intensity in the case of a crystal in which the atoms are in simple cubic array is of the form

$$(1)\ \mathrm{I} \propto e^{-\mathrm{P}(1-\cos\theta)\phi(x)/x}, \qquad \text{or } (2)\ \mathrm{I} \propto e^{-\mathrm{P}(1-\cos\theta)(\frac{1}{4}+\phi(x)/x)},$$

where $\mathrm{P} = \dfrac{0{\cdot}571 \times 10^{-12}}{\mathrm{A} \,.\, \mathrm{T}_c \,.\, \lambda^2}$, $x = \dfrac{\mathrm{T}_c}{\mathrm{T}}$, $\phi(x)$ is a calculated function of x, given by

$$\phi(x) = \frac{1}{x}\int_0^x \frac{\xi\, d\xi}{e^{\xi}-1}.$$

A = atomic weight, T is the absolute temperature, and T_c is a temperature peculiar to the substance under consideration, which Debye calls the characteristic temperature.

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* 'Annalen der Phys.,' vol. 43, p. 87 (1914).

In either (1) or (2) we have, if I_1, x_1, T_1, and I_2, x_2, T_2, are corresponding values, that

$$\frac{I_2}{I_1} = \frac{e^{-P(1-\cos\theta)\,\phi(x_2)/x_2}}{e^{-P(1-\cos\theta)\,\phi(x_1)/x_1}} = e^{-P(1-\cos\theta)\,[\phi(x_2)/x_2-\phi(x_1)/x_1]},$$

or since $n\lambda = 2d\sin\theta/2$

$$\frac{I_2}{I_1} = e^{-0{\cdot}571\times 10^{-12}\,.\,n^2\,.\,[\phi(x_2)/x_2-\phi(x_1)/x_1]/[A\,.\,T_c\,.\,2d^2]}. \tag{3}$$

For aluminium A = 27·1, and Debye* gives the value of T_c as 396.

For the (100) planes the spacing $d = 2{\cdot}03$ Å, and for the (111) planes $d = 2{\cdot}34$ Å. Putting in these values, the curves shown dotted in fig. 3 were obtained. It has not been thought necessary to apply the small corrections for the lack of complete homogeneity of wave-length or for the finite breadth of the beam. Although the agreement is quite good for the (222) spectra, there is considerable divergence between the theory and experiment in the case of the (200).

Carborundum.—In fig. 4 the experimental curves for Carborundum are shown. A crystal with a fine (111) face was used, and there was no trace of deterioration even after repeated heatings to over 900° C. Observations were made, first with the temperature rising slowly, then with gradual cooling. The temperature was measured by means of a platinum-iridium thermocouple enclosed in a fine transparent silica tube placed immediately above the crystal. With this arrangement the lag of the couple was found to be very small.

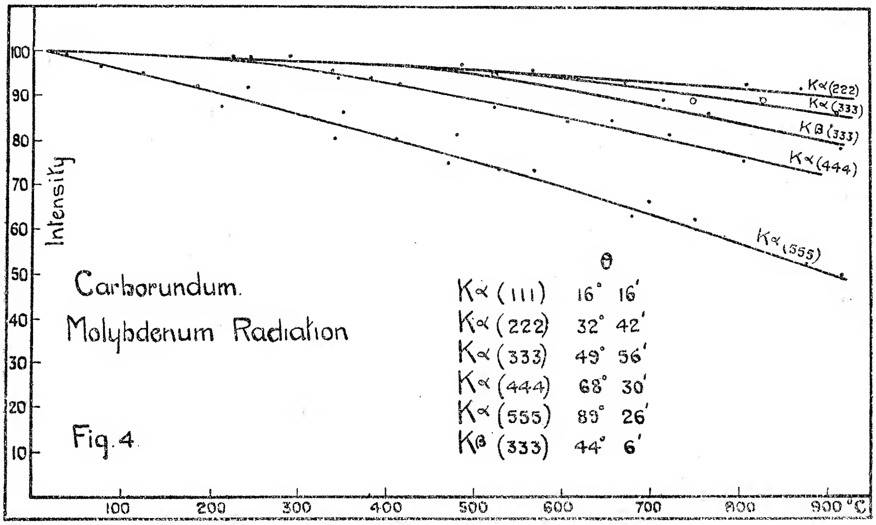

Fig. 4

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* 'Annalen der Phys.,' vol. 39, p. 812 (1912).

The electric heater used for aluminium was unsuitable for temperatures over 600° C., and considerable time was spent in trying various forms of electric furnaces in order to extend the temperature range. The experimental difficulties were peculiar in that the furnace had to be very small and yet had to produce a uniform high temperature in the neighbourhood of a crystal less than 3 cm. from the large brass table of the spectrometer. At the same time, it was necessary to have in the furnace wall opposite the crystal two windows for the ingress and egress of the rays, nothing more than very thin mica being permissible for the windows, on account of the necessity for reducing absorption of the rays to a minimum. In addition to this, the furnace had to be capable of attaining a high temperature quickly, as it is impossible to ensure the constancy of the X-ray emission over a protracted period. Ease of control of the actual temperature was also necessary. Furnaces using mixtures of metallic oxides or graphite as resistances gave high temperatures which were hard to control; also it was difficult to avoid local over-heating. Wire-wound furnaces offered the only practicable solution. Molybdenum winding was not tried, owing to the apparent difficulty of making such a furnace with mica windows sufficiently gas-tight for the use of a hydrogen atmosphere. Nichrome winding was evidently the most suitable, but, on account of the rather low melting-point of this material, a high temperature gradient between the winding and the interior of the furnace had to be avoided, so that a silica core was not permissible. The furnace that was found satisfactory was constructed as follows:—

A tube was made of alundum $1\frac{1}{8}$ inch internal bore, 8 cm. long, and 3 mm. thick; two windows were cut in it for the ingress and egress of the X-rays. The lower end was recessed, and a spiral groove of 1 mm. depth and 2·5 mm. pitch made throughout its length, a hole being bored near either end into which nickel rods could be bolted. The nichrome wire was wound red hot into the spiral and passed at the ends through the nickel rods, the latter keeping the wire in position and serving as terminals. The whole of the nichrome winding, and outside of the tube, was then covered with alundum cement, dried and baked until the cement matured. In this way the whole of the heating element was enclosed (thus reducing risk of oxidation or corrosion) in a chemically very inert substance which, although a good electrical insulator even at high temperatures,* is at the same time a comparatively good heat conductor. Nichrome wire of heavy gauge was used to lead the current to the nickel rods, and in this way corrosion of terminals entirely avoided. The alundum tube was held in position by the three recesses at the lower end, which fitted over narrow steel projecting pieces of the open-work steel base of the outer steel cylinder. Loss of heat by conduction through the frame was thus reduced to a minimum. The space between the core and the outer enclosing cylinder was lagged with magnesium oxide, asbestos being used only where absolutely necessary. Asbestos sheets were used to separate the furnace case and spectrometer table and magnesium oxide to protect the latter from the interior of the furnace. The top of the furnace was closed by four sheets of asbestos board, protected by an asbestos high-temperature compound. With this furnace a current of under 4 ampères (42 watts) produces a rise of temperature of 850° C. in three-quarters of an hour, and over 900° C. in 1 hour.

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* Electric resistivity of alundum is 1·8 megohm-cms. at 1020° C., and of alundum cement, 6000 ohm-cms. at 1100° C. See E. F. Northrup, 'Met. and Chem. Eng.,' vol. 12, p. 125 (1914), and Hering, 'Met. and Chem. Eng.,' vol. 13, p. 25 (1915).

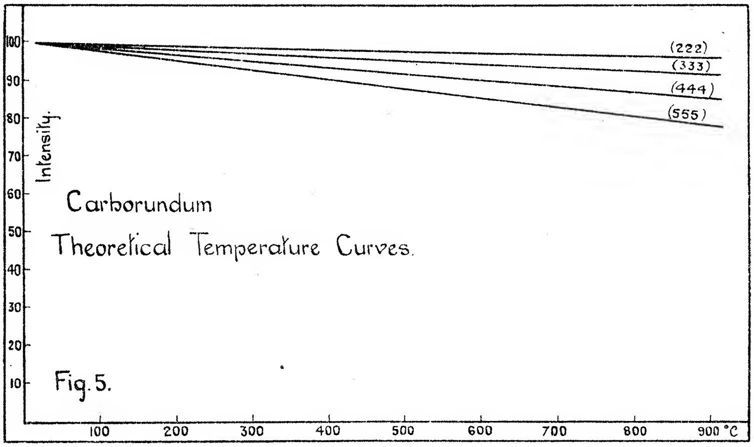
A metallic mounting could not be used for the crystal on account of the rapid conduction of heat through the metal. The mounting adopted consisted of a narrow alundum cylinder surmounted by fire-clay in which the crystal was set.

The points shown in the case of carborundum represent single observations, each the result of rotating the crystal uniformly through 1°, with the ionisation chamber fixed. The alteration of θ with temperature was very small, being only approximately 40 minutes for the Kα (555) spectra at 900° C. Below are given some of the deflections obtained :—

Temperature (t° C.).	Deflection (δ).	Intensity (I).
Kα (222)—		
15	21·2	100·0
292	20·9	98·6
413	20·3	95·8
490	20·7	97·6
565	20·2	95·3
671	19·6	92·5
827	18·9	89·1
872	19·4	91·5
Kα (444)—		
16	23·0	100·0
246	22·7	98·7
337	22·0	95·7
523	20·1	87·4
605	19·3	83·9
719	18·7	81·4
808	17·3	75·0
Kα (555)—		
15	6·1	100·0
213	5·3	86·9
411	4·9	80·4
679	3·8	62·3
912	3·0	49·2

The deflections tabulated are proportional to the intensity of the characteristic radiation only, the deflection for the heterogeneous radiation in each case having been subtracted. In the case of the fourth and fifth orders, however, the amount of the latter was exceedingly small.

It will be seen from the figure that the temperature effect on the intensity becomes rapidly more marked as the value of θ increases; considerably more so than the theory for regular crystals would lead us to expect. If the theory, as it stands, be applied to carborundum, the curves shown in fig. 5 are obtained. They were calculated as follows:—



Carborundum
Theoretical Temperature Curves.

Fig. 5.

The specific heat of carborundum at low temperatures has been determined by Paul Günther,* and taking his value for the molecular heat at 73·5° absolute, *i.e.*, 0·442, we have for the ratio

$$\frac{\text{Molecular heat at } 73{\cdot}5}{\text{Maximum molecular heat}} = \frac{0{\cdot}442}{2 \times 5{\cdot}995} = 0{\cdot}03711.$$

From a Table which Debye† gives showing the values of $1/x$ for values of the above ratio, we have:—

$$1/x = 0{\cdot}0775 \text{ and } \mathrm{T}_c = \frac{73{\cdot}5}{0{\cdot}0775} = 949.$$

By inserting this value for the characteristic temperature of carborundum in expression (3), together with the values $\mathrm{A} = 40{\cdot}3$, $d = 2{\cdot}54$ Å., the curves shown in fig. 5 have been calculated. As will be noticed, it follows from the theory that the curves for the different orders of the same plane should remain unaltered with change of wave-length; for example, Kα (333) should give the same curve as Kβ (333). Referring to fig. 4, it will be seen that a difference exists which, on the whole, seems rather greater than could be accounted for by experimental error.

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* 'Annalen der Phys.,' vol. 51, p. 840 (1916).

† 'Annalen der Phys.,' vol. 39, p. 803 (1912).

Graphite.—In figs. 6, 7 and 8 the (0001) spectra of graphite for molybdenum $K\alpha$-radiation are shown in the order of experiment. Since it was necessary to pass a slow stream of nitrogen through the furnace, in order to prevent oxidation of the graphite, the temperature range was somewhat reduced. It will be noticed that the temperature increase of 850° C. produced an alteration in θ of approximately 17 minutes. This corresponds to an average coefficient of expansion of $26{\cdot}7 \times 10^{-6}$, more than three times the largest value obtained by Fizeau* and seven times the largest value obtained by Muraoka.† Much more recent determinations for Acheson graphite by Day and Sosman‡ give $10^{6}\alpha = 0{\cdot}55 + 0{\cdot}0032\,t$, where $\alpha = [1/L]\,.\,dl/dt$ between 0° and 1500° C. For the range 0° to 850° C. this gives $[L - L_0]/L_0 = 0{\cdot}001624$ or an average coefficient of expansion of $1{\cdot}91 \times 10^{-6}$, and would produce an alteration in θ of only 1·21 minutes. The observed value is fourteen times as great as this. The X-ray method of measurement gives the expansion along the axis only; other methods give results which are more or less averages of expansion in all directions in the crystal. Hence it would appear that in graphite the whole expansion takes place in the direction perpendicular to the (0001) plane, and it seems probable that a contraction occurs in that plane. It is difficult to test this directly, since planes in graphite perpendicular to the (0001) give spectra with very indefinite maxima and in close proximity to those given by planes that are considerably inclined to the perpendicular. This is unavoidable on account of the fact that the most uniform graphite is far from being a single crystal; the (111) planes of the small crystals, of which the substance is composed, are more or less parallel to each other, but otherwise the arrangement is irregular. There is sufficient evidence, however, to emphasize

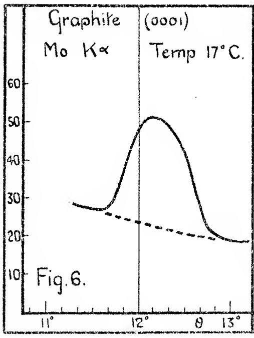

Fig. 6.

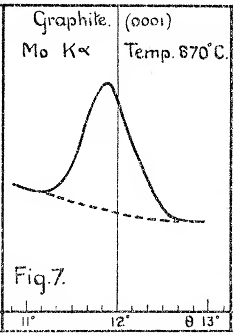

Fig. 7.

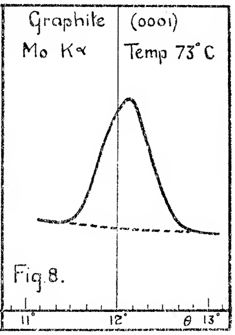

Fig. 8.

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* 'C. R.,' vol. 68, p. 1125 (1869).

† 'Wied. Ann.,' vol. 13, p. 307 (1881).

‡ 'Washington Acad. Sci. Journ.,' pp. 284–289, June 19, 1912.

the weakness of the bonds perpendicular to the (0001) plane compared with those parallel to it. The intensity curve for the (0001) spectra is shown in fig. 9.

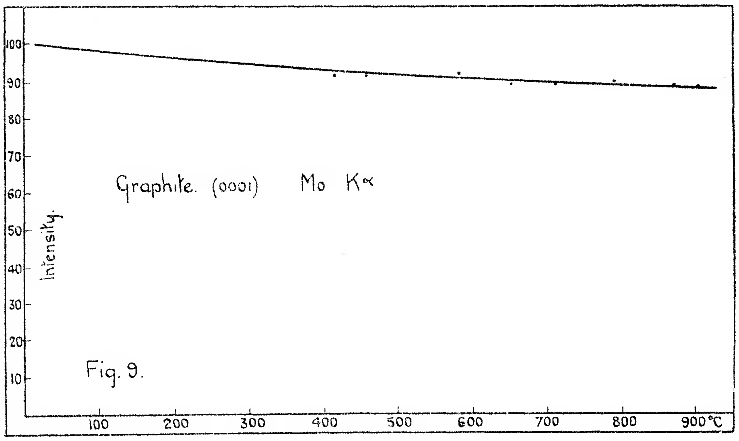

Fig. 9.

Diamond.—Figs. 10 and 11 are examples of curves obtained with the diamond. The alteration of diffraction angle with expansion corresponds to a mean coefficient of $2{\cdot}7 \times 10^{-6}$. The expression found by Fizeau* for the range 10° to 90° C. is

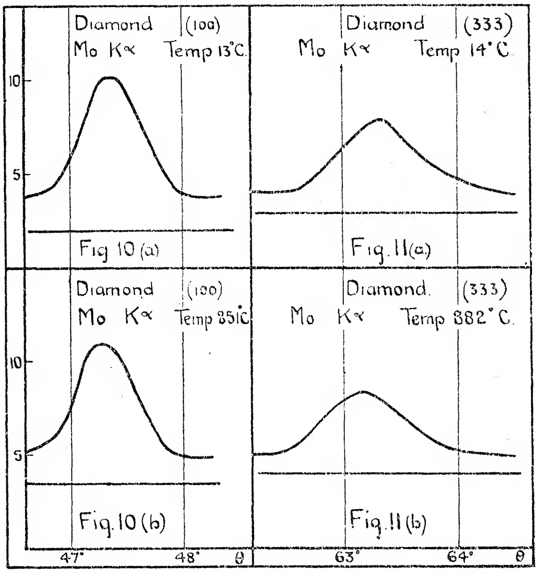

Fig 10 (a)

Fig. 11(a)

Fig. 10 (b)

Fig. 11 (b)

$$L = L_0 (1 + \alpha\theta + \beta\theta^2),$$

where $\alpha = 0{\cdot}60 \times 10^{-6}$ and $\beta = 0{\cdot}72 \times 10^{-9}$.

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* 'C. R.,' vol. 68, p. 1125 (1869).

If Fizeau's formula were assumed to hold over the range of these experiments, viz., 14° to 882° C., the mean coefficient would be $6{\cdot}8 \times 10^{-6}$, much greater than that actually found.

No change in intensity that could be measured with certainty was found for any of the spectra investigated, although in the case of the (333) peak a slight diminution was indicated. The intensity measurements, however, showed that the change was of the order of experimental error, viz., about 2 per cent.

Since the bonds between the carbon atoms in diamond must be exceptionally strong, a very small thermal agitation is to be expected, and fig. 12 shows the small variation of intensity that should exist according to the theory of Debye. Even so, the variation as determined by experiment is considerably smaller.

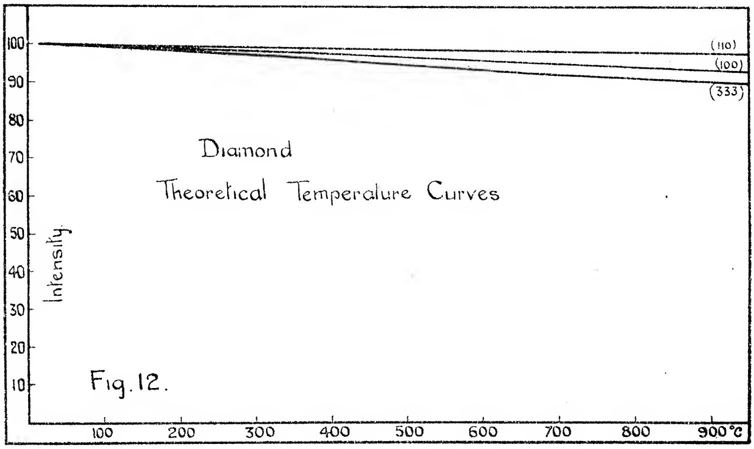

Fig. 12.

The diamonds experimented on were small and completely bathed in the incident beam of rays. The crystal itself was mounted in alundum cement held in a steel cup 4 mm. in diameter, which could be rotated about a vertical axis relative to the vertical segment of a circle to which it was attached, the latter sliding in another circular segment and so capable of rotation about a horizontal axis passing through the centre of the crystal. The whole of the steel mounting was little more than a centimetre high and was cemented to a fireclay cylinder. In this way a very considerable freedom of movement of the crystal was obtained, so that any plane could be brought into position without any part of the mounting interfering with the direct beam. The fireclay foundation was necessary to prevent rapid loss of heat by conduction. A nitrogen atmosphere was used in the furnace.

Ruby and Sapphire.—The curves obtained for the ruby and sapphire are shown in fig. 13, and are of special interest as being the first attempt to examine the behaviour of a crystal which is not cubic, but possesses only the symmetry of the trigonal system. It will be noticed that, while the change in intensity for the $(1\bar{1}0)$ spectra is very small, that for the $(2\bar{2}0)$ is large, also that the intensity of the (111) spectra falls off more rapidly than the (222). This apparently anomalous behaviour can, however, be explained by assuming that the distance between the centres of the aluminium atom pair remains constant and equal to the diameter of the aluminium atom during the expansion of the crystal. It can be shown that the distance (γ) between the centres of the pair of Al atoms is 2·73 Å.U., since the value for the intensity ratio of the 1st to the 2nd order spectra of the (111) plane, calculated on this assumption, agrees with that experimentally determined at normal temperature. Moreover, the relative intensity of the two orders changes very rapidly as γ changes, enabling the latter to be determined with great precision. This is shown in the following Table* :—

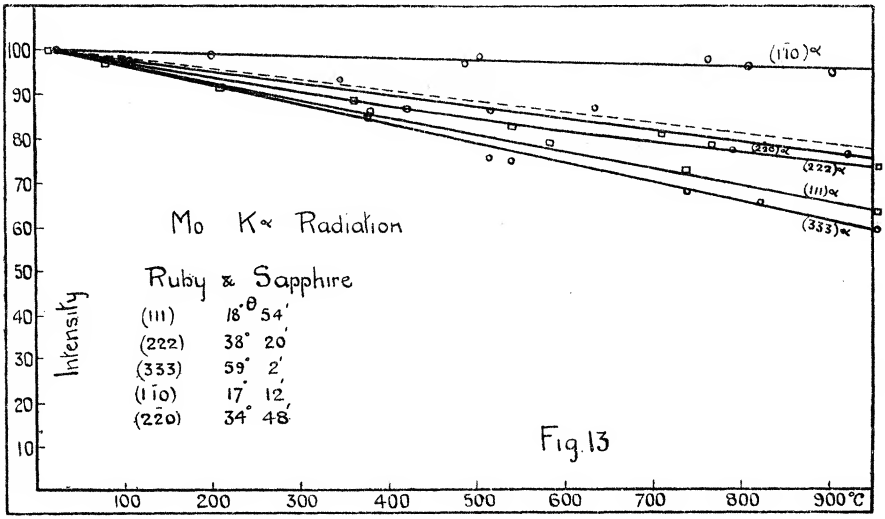

Fig. 13

γ	Amplitude on arbitrary scale.		Expected relative intensity.
	1st order.	2nd order.	
2·86	19·8	25·8	1·7
2·76	13·7	39·8	0·47
2·66	8·5	55·0	0·096
2·5	0	79·1	0

The relative intensity at room temperature is 0·33 (correponding to $\gamma = 2{\cdot}73$).

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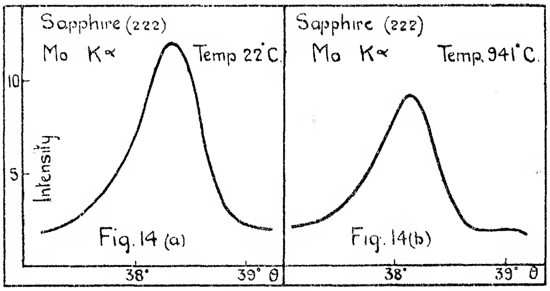
* I am indebted to Sir William Bragg for these figures.

The decrease in this value observed with rise of temperature could be produced by a decrease in γ, or a proportionate increase in the plane spacing.

The mean coefficient of expansion, as deduced from the observed spectral shift in fig. 14, is $5{\cdot}01 \times 10^{-6}$, and would, therefore, increase the spacing between 15° and 950° C. in the ratio of 1·00469 : 1. Dividing 2·73 by 1·00469 we obtain 2·717, and for this value of γ the relative intensity is 0·27, or 82 per cent. of its previous value. Hence it follows that, if the atom pair remain in contact during the expansion of the crystal lattice, the relative intensity of the 1st and 2nd orders at 950° C. is only 82 per cent. of what it would have been had the distance between the pair centres increased proportionally with the lattice. In the latter case the (111) curve would lie in the normal manner above the (222) curve, and, assuming this curve to be unaltered, would lie in the position shown dotted. The exactness of the coincidence cannot be real, but it is clear that the temperature effect can be explained by natural suppositions concerning the changes which temperature would make in the relative distances and the positions of the atoms of a non-cubic crystal.



In conclusion, I should like to express my thanks to Sir William Bragg for the kind interest he has taken in this work, and to the Department of Scientific and Industrial Research for their grant in aid of the same.

Summary.

In the present investigation Prof. W. H. Bragg's early work has been extended to a variety of crystals and higher temperatures. General agreement only is found with the theories of C. G. Darwin and P. Debye.

Aluminium.—A very marked decrease in intensity was observed with rise of temperature, and fair agreement with P. Debye's theory obtained for the (100) and (222) spectra.

Carborundum.—A special furnace was constructed for temperatures up to 960° C. and no deterioration of the crystal was observed. The decrease in intensity with rise of temperature was much greater for the higher order

spectra, and different curves were obtained for the Kα (333) and Kβ (333) spectra.

Graphite.—Only for the cleavage plane reflection was it possible to obtain a definite temperature-intensity curve, and for the direction perpendicular to this plane an unusually high coefficient of expansion was measured.

Diamond.—No decrease in intensity was found that could be measured with certainty, and a very small thermal agitation would be expected on account of the diamond structure's great strength.

Ruby and Sapphire.—An anomalous effect was observed, since the decrease of intensity of the (111) spectra was greater than that of the (222). This may be completely explained by assuming that the atoms of the aluminium pair remain in contact and do not share in the expansion of the lattice.

An Investigation of the Colour Vision of 527 *Students by the Rayleigh Test.*

By R. A. Houstoun, D.Sc., Lecturer on Physical Optics in the University of Glasgow.

(Communicated by Prof. A. Gray, F.R.S. Received June 10, 1922.)

Lord Rayleigh discovered, in 1881,* that if homogeneous yellow is matched with a mixture of homogeneous red and homogeneous green, some persons require much more red, others much more green, in the mixture than the normal. The former have been called red anomalies, the latter green anomalies, and both together have been grouped under the name of anomalous trichromats, because, according to Rayleigh, they are generally not dichromats. Rayleigh obtained matches for 23 male observers. Of these 16 agreed with himself within the errors of observation, and were regarded as normal. Five of the remainder were green anomalies and two red anomalies. Among seven female observers there was not one whose colour vision differed sensibly from his own. Rayleigh did not publish his data, but states that one of the green anomalies had the ratio green to red 2·09 times as great as himself, and one of the red anomalies had the ratio red to green 2·6 times as great as himself. He states that, although the number of observers is insufficient for statistical purposes, it is evident

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* 'Nature,' vol. 25, p. 65 (1881).